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DEVELOPMENT OF HME LAMINATING RESIN

TRW SYSTEMS GROUP

OCTOBER 1975

TECHNICAL REPORT AFML-TR-75-194
FINAL REPORT FOR PERIOD MAY 1974 - AUGUST 1975

AIR FORCE MATERIALS LABORATORY
AIR FORCE WRIGHT AERONAUTICAL LABORATORIES
Air Systems Command
Wright-Patterson Air Force Base, Ohio 45433

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This technical report has been reviewed and is approved for publication.

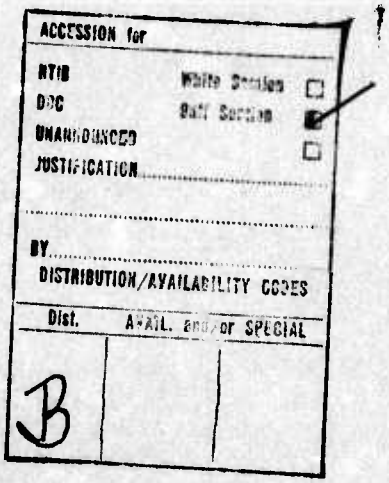
C. E. Browning

C. E. BROWNING,
Project Monitor

FOR THE COMMANDER

T. J. Reinhart, Jr.

T. J. REINHART, JR., Chief
Composite and Fibrous Materials Branch
Nonmetallic Materials Division



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The HME resin formulation and synthesis procedure were optimized to yield a stable resin. Composite and honeycomb sandwich panels were vacuum bag molded and provided low resin flow during cure. The resultant composite and sandwich panels demonstrated excellent moisture resistance and suitability for service at 275°F. Also the cocured sandwich panels provided equivalent flatwise tensile strength values to secondary bonded panels.

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FOREWORD

This report was prepared by TRW Systems Group, Redondo Beach, California, under Contract F33615-73-C-5094, "Development of Low-Flow, Low Pressure Cure Laminating Resin System". The contract was initiated under Project No. 7340, Task L, and administered under the direction of the Air Force Materials Laboratory, Wright-Patterson Air Force Base, with Mr. C. Browning (AFML/MBC) composites and Fibrous Materials Branch, Non-metallic Materials Division, as the Project Engineer. Mr. R. W. Vaughan, Program Manager, directed the program at TRW Systems. Dr. G. A. Zakrzewski was responsible for the experimental activities assisted by Mr. K. Ueda. Mr. C. Sheppard provided significant guidance in resin formulary. TRW Systems program administrative and review personnel were Mr. R. Hammel and Mr. B. Dubrow.

The report covers the period from 1 May 1974 through 31 August 1975 and was submitted for review in August 1975.

A previous report, AFML-TR-74-134, covers the period from 1 May 1973 through 30 April 1974.

The Contractor's report number is 24231-6029-TU-00.

The mention of commercially available products should not be construed in any way as an endorsement by the Government. Comparative information has been presented for the purpose of illustrating the influence of processing parameters on various materials and their properties.

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I. INTRODUCTION

This final report presents the work accomplished by TRW Systems for the Air Force Materials Laboratory, Nonmetallic Materials Division, Air Force Systems Command, USAF, Wright-Patterson Air Force Base, Ohio, under Contract F33615-73-C-5094 during the period 1 May 1974 through 31 August 1975. The objective of this program was to develop a low-flow laminating resin suitable for fabricating high performance composites and cocured sandwich panels by vacuum bag molding.

The work described in this document was a continuation of that previously reported (Reference 1) during which two approaches were investigated for providing a low-flow, low pressure cure laminating resin. These two approaches were: 1) epoxy resins modified with high 1,2 vinyl content polybutadiene (HME resin) and 2) aromatic amide or ester resins curing through novel end-caps (DONA) developed under Contract F33615-72-C-2122 (Reference 2). After preliminary evaluation of these two approaches, the HME resin was selected as the most promising. This resin provided Hercules A-S graphite fiber reinforced composites that were vacuum bag molded, had low resin flow during molding, possessed good fiber orientation and demonstrated good potential for providing mechanical properties equivalent to those obtained with autoclave molded state-of-the-art epoxy resin systems. Another key feature of the HME resin composites was their excellent moisture resistance. This was demonstrated by the high strength retention of HME/A-S composites after 30 days exposure in a high humidity environment. The success of the HME in providing the unique combination of vacuum bag processability, low resin flow and high moisture resistance is attributed to the high 1,2 vinyl content polybutadiene segment of the HME resin. The epoxy-polybutadiene elastomeric prepolymer for the HME resin (B-staged prepreg) is a very low viscosity liquid at ~350°F. At this temperature, rapid resin gelation occurs as a result of homopolymerization of the pendant vinyl groups. Thus, vacuum bag molding is possible because of the resin's low viscosity at 350°F and concurrently low resin flow occurs because of the short gel time of the resin at 350°F. Retention of mechanical properties after high moisture exposure occurs due to the hydrophobic character of the polybutadiene resin.

The work described in this report addressed two technical objectives:

- Optimize the HME resin to provide reproducible composite properties, and
- Demonstrate the suitability of the HME resin for fabricating cocured sandwich panels by vacuum bag processing.

During this work it was demonstrated that excellent reproducibility is obtained by first preparing an HME prepolymer and then coating the reinforcement. This was initially demonstrated in work performed in-house at AFML. The previous work (Reference 1) had used a solution of resin ingredients to coat the reinforcement which then was B-staged *in situ*. This earlier approach had not provided consistent results. The reproducibility of the HME resin prepared as a prepolymer was demonstrated by the results obtained from testing vacuum bag molded, unidirectional and multidirectional HME/A-S composite panels. Vacuum bag molded, cocured honeycomb sandwich panels were fabricated from the HME resin which provided high strength skins and good adhesion of the skins to the aluminum alloy honeycomb core.

TRW Systems conducted the earlier work as Tasks I, II and III (Reference 1) and the continuation activities described in this report were conducted as three additional tasks, *i.e.*, Tasks IV, V and VI. This report is divided into sections covering the two key activity areas:

- HME Resin Optimization, and
- Panel Fabrication and Evaluation.

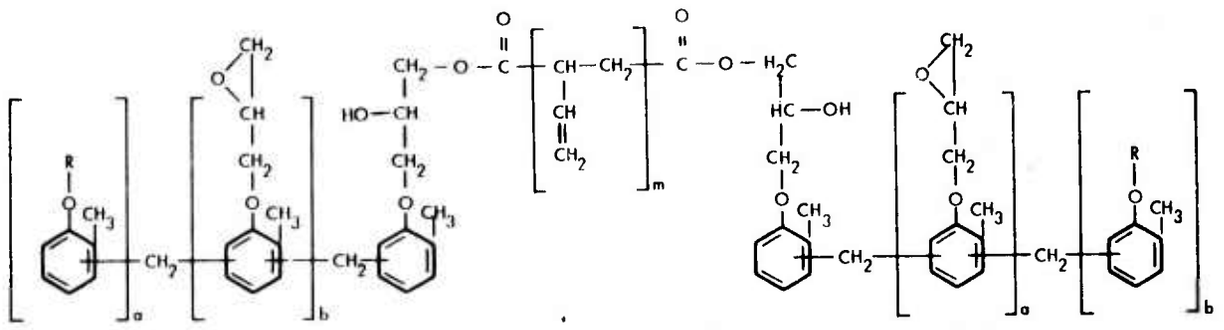
Details regarding the selection of resin ingredients, reaction kinetics studies, formulation screening and HME resin preparation procedures are provided in Section II. Composite and sandwich panels fabrication procedures are described in Section III, along with test results from evaluation of both composite and sandwich panels. The significant conclusions reached and assessments of the results are listed in Section IV, together with recommendations for activities that warrant further investigations. Detailed test procedures used during this program are described in the appendices.

II. HME RESIN OPTIMIZATION

Evaluation of HME resin during Tasks I, II and III (Reference 1) demonstrated the suitability of this resin for fabrication of structural high performance composites by vacuum bag molding. During molding, very low resin flow occurs, which is attributed to a short gel time. This is preceded by a significant resin viscosity reduction, which contributes to excellent fiber wetting and ply consolidation. Key features displayed by HME resin composites are suitability for service ~250 to 300°F and high resistance to moisture degradation. The work described in this section was concerned with optimization of the HME resin formulation and preparation procedures, in order to ensure resin reproducibility to provide acceptable strength retention at elevated temperatures. Modification of the HME resin formulation to provide crack-free pseudo-isotropic composite panels also was accomplished by addition of a tough, elastomeric segment to the resin. Specific subjects addressed include resin constituent selection, reaction kinetics, formulation screening and HME resin preparation.

2.1 RESIN CONSTITUENT SELECTION

The HME resin consists of a high 1,2 vinyl content polubutadiene end-capped with a high performance epoxy resin (see Structure 1).



Use of the high 1,2 vinyl content polybutadiene to modify high temperature epoxy resins provides several key features. These include vacuum bag processability and excellent moisture resistance. The unique processing characteristics of the HME resin is attributed to the low viscosity of the epoxy-polybutadiene elastomer at 350°F, which is followed by rapid gelation as vinyl homopolymerization occurs. Because the polybutadiene

resin is hydrophobic, the HME resin is resistant to moisture degradation.

The requirements applied to the selection of a specific polybutadiene resin for use in the HME resin formulation were:

- The polybutadiene resin had to contain end-caps suitable for reaction with epoxy resins.
- A short chain length between cross-link sites was required in order to maintain mechanical properties at elevated temperature.
- High 1,2 vinyl content was required in order to obtain the initial rapid cure via vinyl polymerization (Reference 3).

Consequently, a HYSTL polybutadiene resin was selected because the HYSTL resins are the only available high 1,2 vinyl content end-capped resins. The HYSTL C1000 resin was selected from the HYSTL resin product line because it provided the lowest average molecular weight (about 1000) and contained carboxyl end-caps which react with epoxy resins.

Similarly, there were specific requirements which guided the selection of epoxy resins for use in the HME resin formulation. These requirements were:

- High functionality to yield an intense cross-link network
- Solubility in a common solvent with the polybutadiene resin
- Cure ~350°F to provide compatibility with the vinyl polymerization
- Suitability for 300 - 350°F service.

The epoxy novalac resins possess the highest functionality of the commercially available epoxy resins. Consequently, evaluation of epoxy resin was limited to phenolic and cresol novalac epoxy resin. Candidate

resins selected for evaluation are shown in Table 1. Discussion of the selection of a specific epoxy resin is provided in Section 2.3.

TABLE 1.
CANDIDATE EPOXY RESINS

Resin	Functionality	Type
DEN 431	2.2	Phenolic Novalac
EPN 1238	3.8	Phenolic Novalac
DEN 438	3.8	Phenolic Novalac
ECN 1273	4.8	Cresol Novalac
ECN 1280	5.1	Cresol Novalac

During the formulation screening studies (see Section 2.3), it was shown that the basic high 1,2 vinyl polybutadiene epoxy resin copolymer was too brittle for use in multidirectional graphite fiber composites. Consequently, a high 1,4 (low 1,2) vinyl content polybutadiene resin was evaluated as a means of providing improved toughness. Blending the low 1,2 vinyl content resin with the C1000 resin provided elastomeric segments to the cured HME resin because there are significantly fewer pendant vinyl groups available for homopolymerization. A commercially available hydroxyl end-capped high 1,4 vinyl content polybutadiene (ARCO 45 HT) was selected for evaluation.

The catalyst used to promote vinyl polymerization during initial cure of the HME resin is an organic peroxide compound. It was established previously (Reference 1) that the peroxide catalyst should have a half-life at 350°F of one to two minutes. Several commercially available peroxide catalysts were considered (see Table 2) from which Lupersol 101 was selected, because the half-life was closest to the target of one to two minutes.

TABLE 2.

CANDIDATE PEROXIDE CATALYSTS

Description	Half-Life, at 350°F, Minutes
Dicup (dicumyl peroxide)	0.41
t-Butyl perbenzoate	0.38
Lupersol 101 (2,5-dimethyl-2,5-di-*t*-butylperoxy hexane)	0.98
di-*t*- butyl peroxide	5.16
Lupersol 130	4.08

Another catalyst was required to promote the epoxy-carboxy reaction during prepolymer preparation. Cordova Chemical AMC-2 was selected for this purpose because it is commercially available and is a specific catalyst for this reaction. Its suitability was initially demonstrated in work performed in-house at AFML. Details of the use of these catalysts are provided in Section 2.1. Benzyldimethylamine (BDMA) was chosen as the epoxy hardener for the final cure because it promotes the desired epoxy homopolymerization. Other epoxy hardeners and extenders probably are suitable but none have been evaluated so far during this program.

During the previous work and during the formulation screening studies, *bis*(4-maleimido phenyl) methane (BMPM) was evaluated as a cross-linking agent for the vinyl double bonds. However, during further evaluation, BMPM did not appear to enhance the properties of cured HME resin. Details of the evaluation of formulations containing BMPM are provided in Section 2.3.

2.2 REACTION KINETICS

Procedures for preparing an HME prepolymer were studied in order to obtain a shelf stable HME resin that provided reproducible composite panel properties. This approach was considered the most viable route to attaining good resin reproducibility and was necessary because it was observed previously that resin advancement occurred during storage (Reference 1). In order to establish the correct prepolymer preparation procedures, reaction kinetics studies were performed.

The first study evaluated the effect of various HME resin constituents (see Table 3) on reaction time during prepolymer preparation. These studies showed that the reaction occurs more rapidly if BMPM is not used and also that the reaction rate is more rapid if AMC-2 catalyst is used instead of BDMA (see Figure 1). It was expected that the AMC-2 catalyst would increase the reaction rate because it is a specific catalyst for the epoxy-carboxy reaction. This was demonstrated by comparing viscosity *vs* time plots for epoxy resin ECN 1280 catalyzed with BDMA and AMC-2 (see Figure 2). These plots clearly indicate that the AMC-2 catalyst is specific for the epoxy-carboxy reaction and is not effective for promoting epoxy homopolymerization. Further viscosity *vs* time studies then were performed to determine the effect of catalyst concentration on reaction rate (see Table 4 and Figure 3). As was expected, the reaction rate increases significantly with increased catalyst concentration.

TABLE 3.
HME RESIN FORMULATIONS FOR REACTION RATE STUDIES

Constituent	Formulation, pbw				
	A	B	C	D	E
C-1000	50	50	50	50	50
ECN 1280	68	68	68	68	68
BMPM	7.5	-	7.5	-	-
LUPERSOL 101	4.15	4.15	-	-	-
BDMA	1.3	1.3	1.3	1.3	-
AMC-2	-	-	-	-	1.2
MEK	120	120	120	120	120

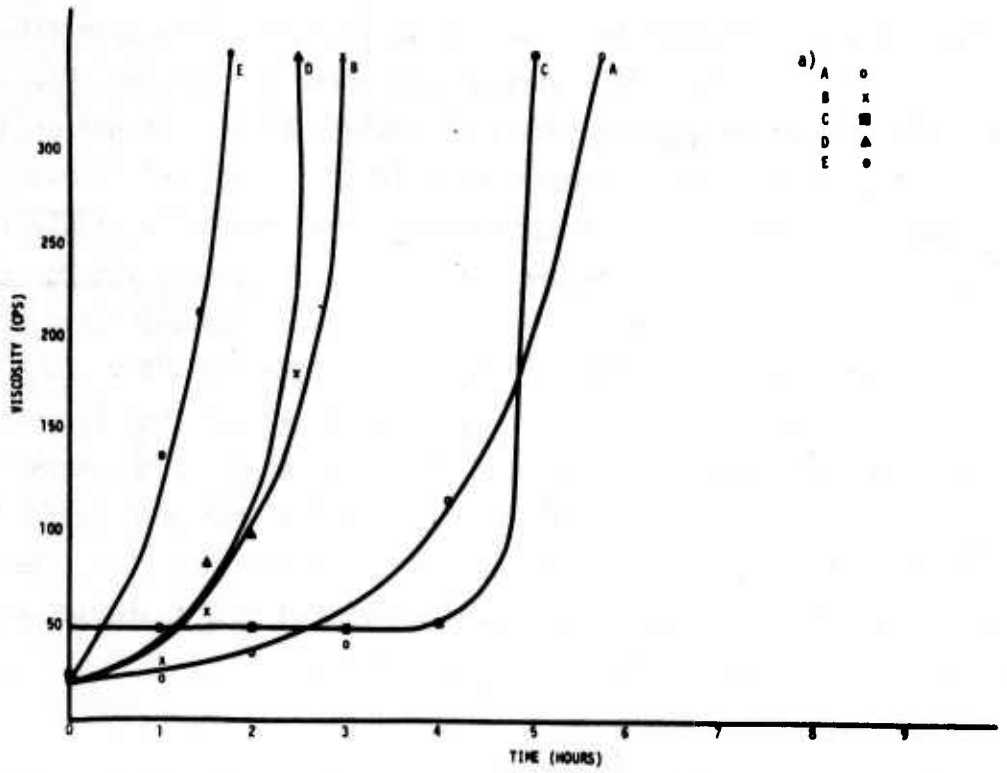


Figure 1. Viscosity *vs* Time - Resin Formulation[a] Studies (in MEK at 176°F)

[a] See Table 3 for resin formulations.

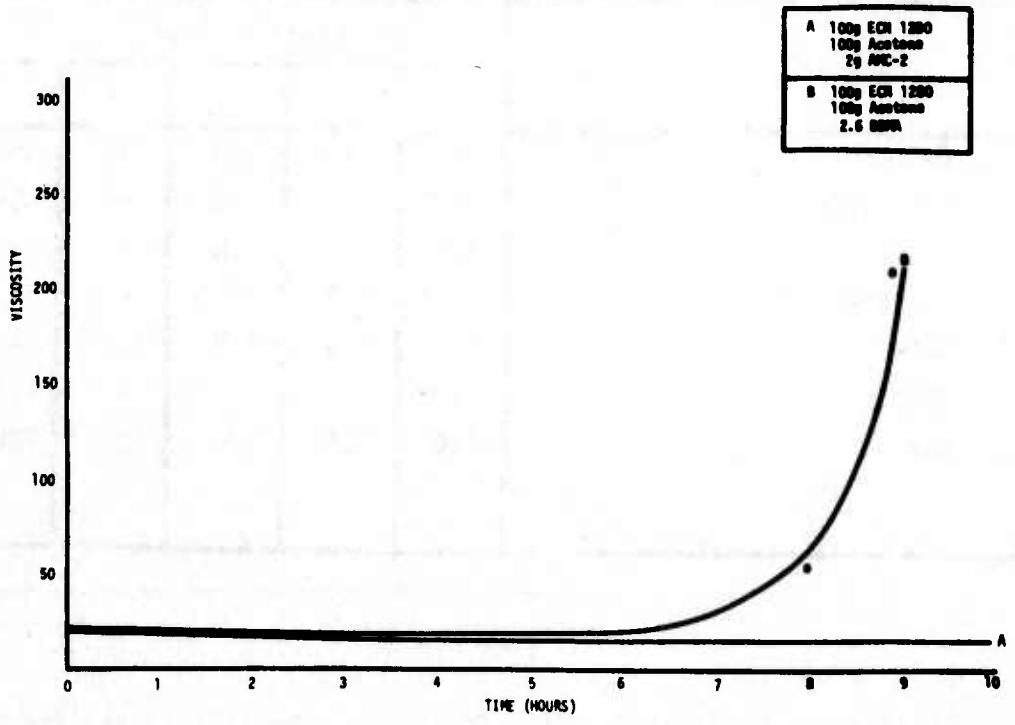


Figure 2. Viscosity *vs* Time For Epoxy Homopolymerization With Different Catalysts (in Acetone at 136°F)

TABLE 4.

EFFECT OF AMC-2 CATALYST CONCENTRATION ON RESIN VARNISH VISCOSITY

Constituent	Formulation, pbw		
	A	B	C
C-1000	33	33	33
ECN 1280	44	44	44
AMC-2	0.3	0.6	1.2
MEK	80	80	80

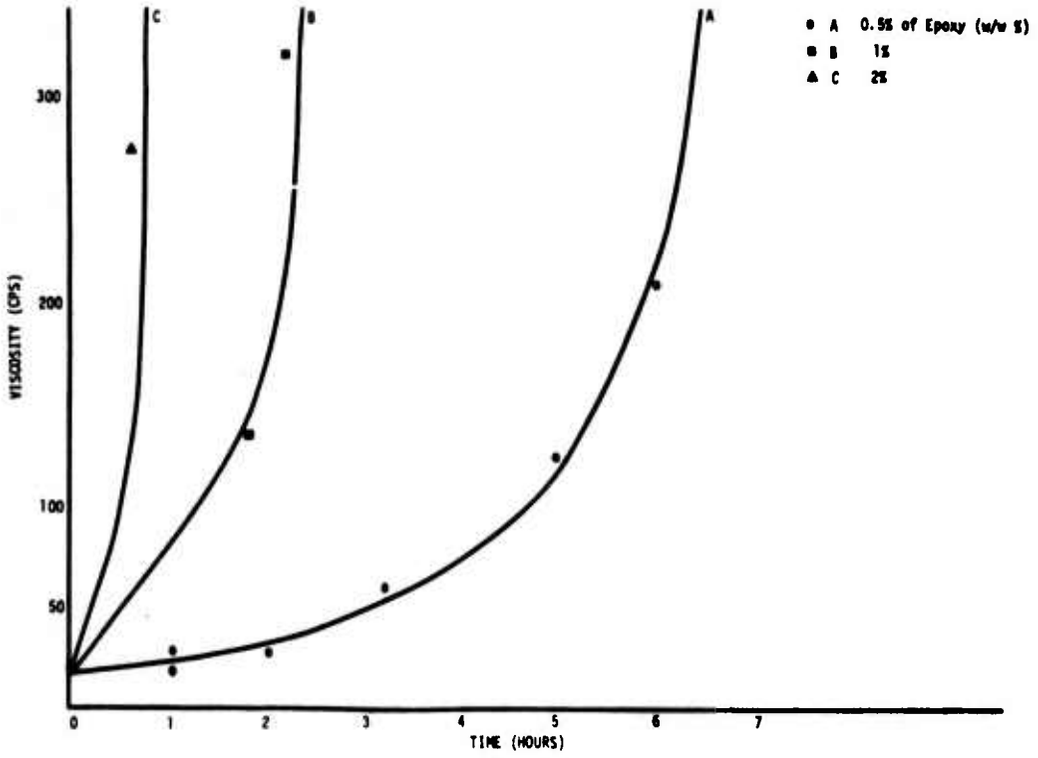


Figure 3. Viscosity *vs* Time For Various AMC-2 Catalyst Concentrations (At 176°F)

Finally, studies were performed to determine the carboxy-epoxy reaction rate for an HME prepolymer. This was accomplished by measuring the acid number as a function of refluxing time. The formulation shown in Table 5, column M was used for these studies with acetone substituted for MEK for the 136°F plot (see Figure 4). It was shown during these studies that the carboxy-epoxy reaction proceeds rapidly in refluxing MEK at 176°F to approximately fifty percent completion after which the rate decreases. The same resin formulation in refluxing acetone at 136°F reacts at a significantly slower rate. These data were used to determine procedures for HME prepolymer manufacture (see Section 2.4).

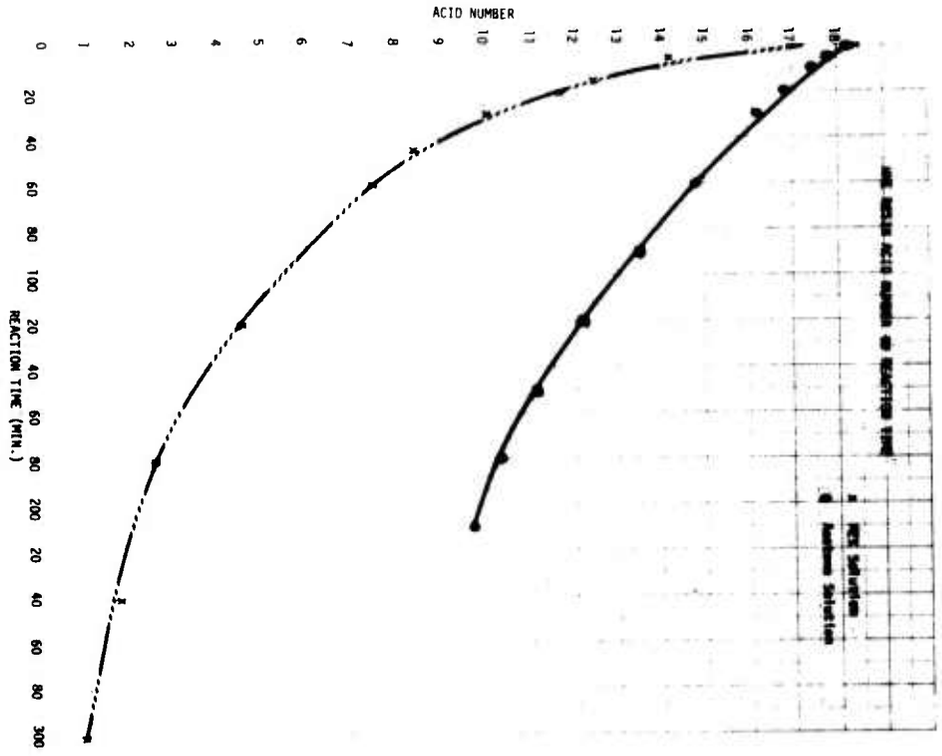


Figure 4. Acid Number *vs* Reaction Time Of HME Prepolymer

2.3 FORMULATION SCREENING

In order to make a final selection of the most promising HME resin formulation for detailed evaluation, prepreg tapes and composites were prepared from candidate formulations (see Table 5). Prepreg tapes were prepared by drum winding at 8 tows per inch, Hercules Type A-S continuous

TABLE 5.

PRE-COOKED RESIN FORMULATION FOR SCREENING

Constituent	Formulation, pbw																
	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q
Constituents for Cooking																	
C-1000PB	100	100	100	100	100	100	100	100	100	100	100	100	80	80	80	100	100
ARCO 45-HT	-	-	-	-	-	-	-	-	-	-	-	-	60	60	60	-	-
ECN 1280	137	137	137	137	137	137	137	137	137	137	137	137	137	137	137	-	137
AMC-2	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.6	2.6	2.6	2.6	2.6
ACETONE	-	-	-	-	-	560	-	560	560	560	560	560	-	560	560	560	560
MEK	560	560	580	560	560	-	560	-	-	-	-	-	560	-	-	-	-
Additives to Cooked Resin																	
BMPM	-	-	-	-	15	15	15	15	15	15	-	-	-	-	-	15	-
LUPERSOL 101	8.3	8.3	8.3	8.3	8.3	8.3	8.3	8.3	8.3	8.3	8.3	8.3	8.3	8.3	8.3	5.8	5.8
BDMA	-	-	-	-	-	-	-	-	2.7	2.7	2.7	2.7	2.7	5.4	2.7	2.7	2.7
Triallyl Cyanurate	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	15
Methyl Nadic Anhydride	-	-	-	-	-	-	-	-	-	-	-	-	-	-	15	-	-

graphite fiber impregnated with HME resin varnish. The varnish was cooked for various time periods using MEK and acetone as solvents. A calculated amount of resin varnish was doctored onto the prewound graphite and dried overnight. Composites then were molded by the vacuum bag process using a heat-up rate of 5 - 7°F/minute, a cure temperature of 350°F and a cure time of 60 minutes. After cure, the composites were cooled to room temperature slowly and postcured at 350°F or 400°F for 16 hours. The variables of cooking time, solvent, use of BMPM and postcure temperature were studied first. Results from this study indicated that BMPM is useful in promoting epoxy cure at 350°F, but the resultant properties were lower than expected (see Table 6). An epoxy accelerator then was evaluated to promote postcure. The resultant properties of these composites (see Table 6) indicated that the epoxy accelerator is necessary to obtain good retention of properties at 275°F and 350°F. Composites also were used to evaluate prepreg drying cycles, the use of BMPM, epoxy blends of ECN 1235 with 1280, BDMA catalyst concentration, and the use of triallyl cyanurate and methyl nadic anhydride as additives to increase property retention at 275°F. Prepreg drying does not appear to be a significant factor affecting

TABLE 6.
PROPERTIES OF COMPOSITES MADE USING PRECOOKED RESINS

Experiment	Formulation, pbw																	
	A	B	C	D	E	F	G	H	I[b]	J	K[b]	L	M[a]	N	O	P	Q
Resin Cooking Time	15	60	15	60	15	45	15	45	45	45	45	45	45	45	45	45	45
Resin Solvent	MEK	MEK	MEK	MEK	MEK	ACE-TONE	MEK	ACE-TONE	MEK	ACE-TONE	ACE-TONE	ACE-TONE	MEK	ACE-TONE	ACE-TONE	ACE-TONE	ACE-TONE
BMPM in Resin	No	No	No	No	Yes	Yes	Yes	Yes	Yes	Yes	No	No	No	No	No	Yes	No
BMDA in Resin	No	No	No	No	No	No	No	No	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Postcure Cycles (Hrs/°F)	16/350	16/350	16/400	16/400	16/350	16/350	16/400	16/400	16/400	16/400	16/400	16/400	16/400	16/400	16/400	16/400	16/400
Flexural Strength, Ksi																	
at R.T.	177	183	200	220	172	150	187	172	218	236	242	224	211	183	200	220	190
at 275°F	34	40	68	74	71	41	115	86	124	128	120	120	128	93	100	105	110
Flexural Modulus, Msi																	
at R.T.	-	-	16.0	16.8	-	14.5	15.9	-									
Shear Strength, Ksi																	
at R.T.	8.1	8.6	8.8	8.8	8.2	5.8	8.7	8.6		10.0	8.4	10.7	9.8	4.0	10.3	10.9	6.0
at 275°F	2.5	3.3	6.8	4.7	4.7	3.2	6.2	6.8		-	-	-	-	6.8	5.6	4.8	4.8
at 350°F	-	-	-	-	-	-	-	-		-	-	-	-	3.6	-	4.7	4.3
Fiber Vol, % v/v	55	57	59	57	54	54	59	56									
Density, g/cc	1.46	1.50	1.52	1.46	1.46	1.45	1.50	1.45		1.47	1.49	1.51	1.48	1.51	1.49	1.50	1.49
Void Content, %	4	1	1	4	3	4	2	5		1	3	1	4	1	3	2	3
Resin Content, % w/w	34	33	32	32	35	35	33	32		30	33	34	33	35	35	35	33

[a] 1,2/1,4 PB Blend

[b] Prepreg air dried at R.T., all others dried at 150°F for 30 minutes.

the resultant properties (see Table 6) because panels I and J, as well as K and L provided similar properties. The use of 1,4 polybutadiene blended with 1,2 polybutadiene (composite M) provided a composite panel with excellent properties and good elevated temperature property retention. Doubling the BDMA catalyst concentration (composite N) did not improve the elevated temperature property retention, therefore the BDMA level (2% of total epoxy) used for the other composites was selected. The use of epoxy blends (composite P), addition of triallyl cyanurate (composite Q) and addition of methyl nadic anhydride (composite O) did not improve the properties of composite panels.

Because the properties of the composite panels of formulations L to Q (made using BDMA epoxy accelerator as an additive to the prepolymer varnish) were not significantly different, the final resin selection was based on the photomicrographs of pseudo-isotropic multidirectional panels. These panels were made using the ply configuration of 0°, +45°, -45°, 90°, 90°, -45°, +45°, 0°, with resin formulations L, M, N, O, P, and Q (see Table 5). After fabrication, specimens were machined, potted and polished (see Figure 5). From the photomicrographs, composites containing formulations M and O were shown to contain significantly fewer cracks than the other composites. Because formulations M and O provided composites with similar properties, it was concluded that methyl nadic anhydride does not enhance the properties of cured HME resin and therefore is not required in the formulation. Consequently, formulation M was selected for detailed evaluation.

2.4 HME RESIN PREPARATION

Based on the HME resin formulation screening studies described in Section 2.3, the formulation shown in Table 7 was selected for the HME prepolymer and the formulation in Table 8 for the HME resin. Sources and descriptions of the constituents are shown in Table 9. In preparation of the HME resin, first an adduct is formed by reacting the C1000 high 1,2 vinyl polybutadiene, the ARCO-45-HT high 1,4 vinyl polybutadiene and the cresol novalac epoxy resin (CIBA-GEIGY ECN 1280). This reaction is performed in refluxing MEK (176°F) for 45 minutes. The Cordova Chemical AMC-2 catalyst is used to promote the carboxy-epoxy reaction. After completion of this reaction, the acid number of the HME prepolymer is measured (see Appendix A) to ensure that adequate prepolymerization has occurred, *i.e.*, acid number <10. The epoxy and vinyl homopolymerization catalysts (BDMA and Lupersol 101) then are added to the prepolymer solution.

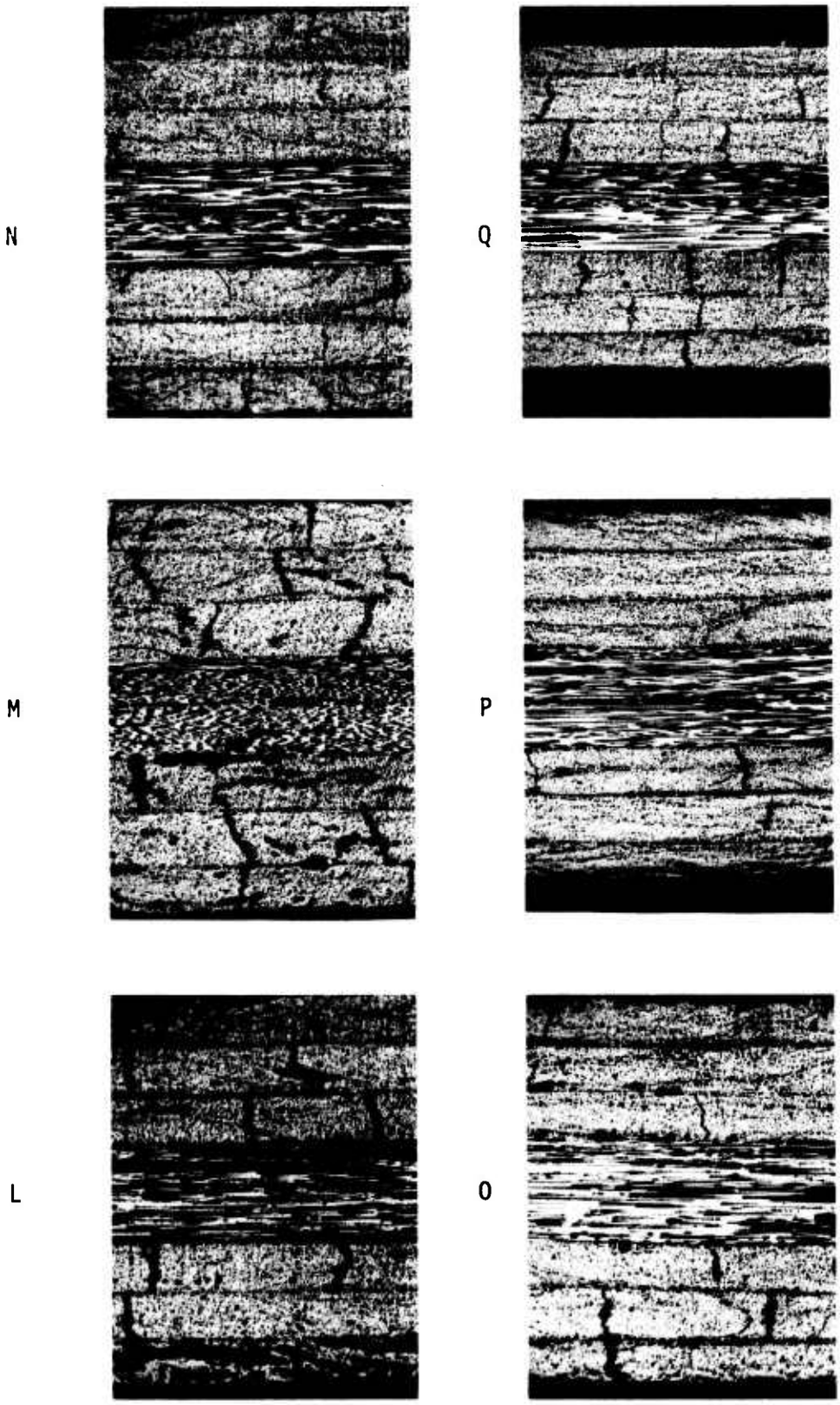


Figure 5. Photomicrographs Of Pseudo-Isotropic Multidirectional Composites (See Table 8 For Formulations)

TABLE 7.

HME PREPOLYMER[a)] FORMULATION

Constituents	pbw
C-1000	80[b)]
ARCO 45 HT	60[b)]
ECN 1280	137
AMC-2	2.6
MEK	560

[a)] Reacted 45 minutes in refluxing MEK (176°F)

[b)] 80/20 Mole % - C1000/45HT

TABLE 8.

HME RESIN FORMULATION

Constituents	pbw
HME PREPOLYMER VARNISH	839.6
LUPERSOL 101	8.3
BDMA	2.7

TABLE 9.

HME RESIN CONSTITUENTS

CONSTITUENT	DESCRIPTION	SOURCE
C-1000	Carboxy terminated polybutadiene, 90% 1,2	Dynachem Corp.
ARCO 45 HT	Hydroxy terminated polybutadiene, 80% 1,4	ARCO Chemical
ECN 1280	Epoxy cresol novalac, Functionality 5.1	CIBA-GEIGY
AMC-2	Epoxy-carboxy accelerator	Cordova Chemical
Lupersol 101	Organic peroxide	Wallace & Tiernan
BDMA	Benzyldimethylamine	Pacific Chemical

III. PANEL FABRICATION AND EVALUATION

Vacuum bag molding procedures were developed for fabricating unidirectional and pseudo-isotropic graphite fiber reinforced composite panels from the HME resin. These procedures then were adapted for fabricating one-stage cocured honeycomb sandwich panels by the vacuum bag molding process. Panels produced during these studies then were tested and were shown to provide significantly higher strength retention values after high humidity exposure than state-of-the-art materials. The initial properties at room temperature and at 275°F prior to high humidity exposure also were equivalent to high pressure, autoclave molded state-of-the-art epoxy composites. Very little skin dimpling on the cocured sandwich panels was observed and adhesion of the HME/A-S skins to the aluminum honeycomb core was excellent. Details of the fabrication procedures and test results are provided in this section.

3.1 COMPOSITE PANEL FABRICATION

Prepreg tape was prepared by drum winding Hercules type A-S graphite fiber tow impregnated with the HME resin MEK solution (see Table 8). The graphite fiber was collimated at eight tows per inch with a resin content of 32 to 33% by weight, *i.e.*, ~60% fiber volume. After drying, the prepreg had a retained volatile matter content of 1 to 2% by weight and the thickness was 0.016-inch. The average yield of prepreg tape was twelve square feet per pound.

Composite panels were fabricated from the HME/A-S prepreg tape by stacking the tapes eight-ply thick, either unidirectionally, or in a 0°, +45°, -45°, 90° symmetrical pattern to provide pseudo-isotropic panels. Nonporous glass reinforced Teflon R coated fabric was placed on the top and bottom of the prepreg stack and 0.002-inch thick Mylar film was laid over the Teflon (see Figure 6). Style 181 glass fabric was laid over the Mylar film as breather material and a nylon film vacuum bag (green Vac-Pak)

was installed over the prepreg stack and sealed to the caul plate with a commercial vacuum bag sealant (Schnee Morehead). Air was evacuated out of the bag down to 28 inches of mercury to provide ∿14 psia molding pressure and the assembly was placed in an air circulating oven. The temperature was raised to 350°F at 3 to 5°F per minute and the panels were cured for one hour at 350°F. Following cure, the panels were removed from the vacuum bag and postcured in an air circulating oven for 16 hours at 400°F.

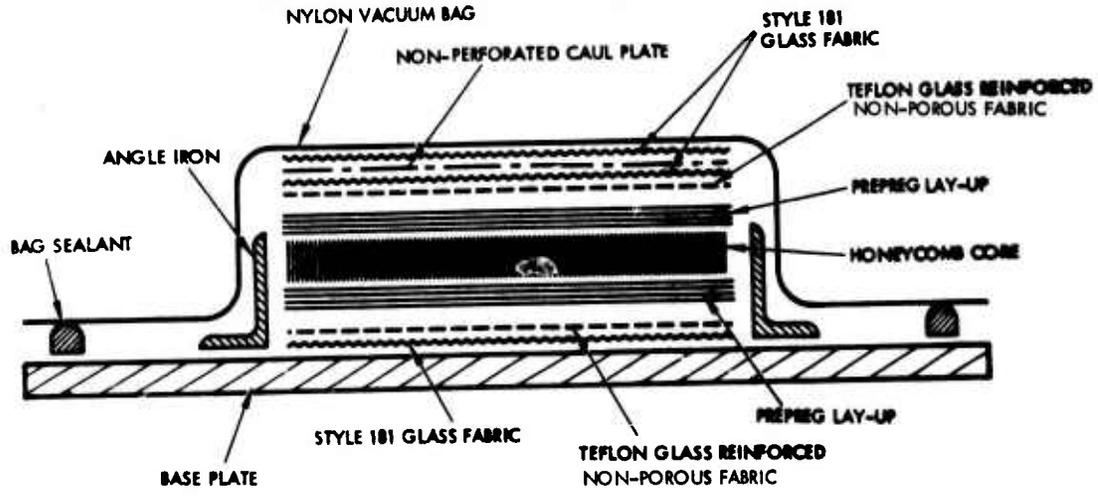


Figure 6. Composite Panel Fabrication

The resultant panels had excellent appearance (see Figure 7) and contained no visible cracks, voids or blisters. Photomicrographs were taken of sections from pseudo-isotropic panel (see Figure 8), which confirmed these observations. Ply thickness for the unidirectional panels was 0.010-inch and the pseudo-isotropic panels ply thickness was 0.012-inch. Mechanical properties measurements then were taken on the resultant panels, as described in Section 3.3.

3.2 HONEYCOMB SANDWICH PANEL FABRICATION

Procedures were developed for fabricating honeycomb sandwich panels consisting of HME/A-S outer skins on Hexcel honeycomb core, CR-III corrosion inhibited, one-eighth inch cell size, 1.5 mil nonperforated 5052

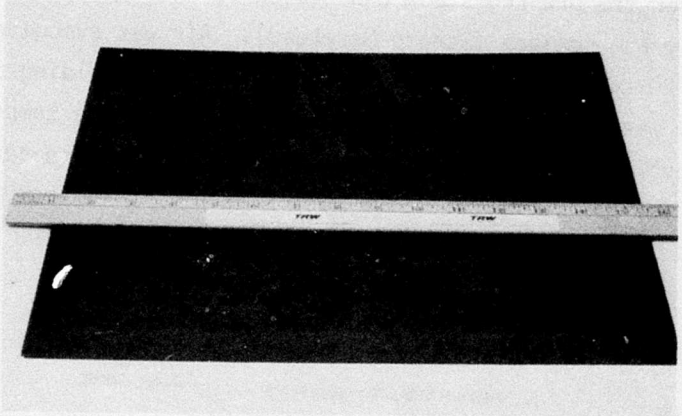
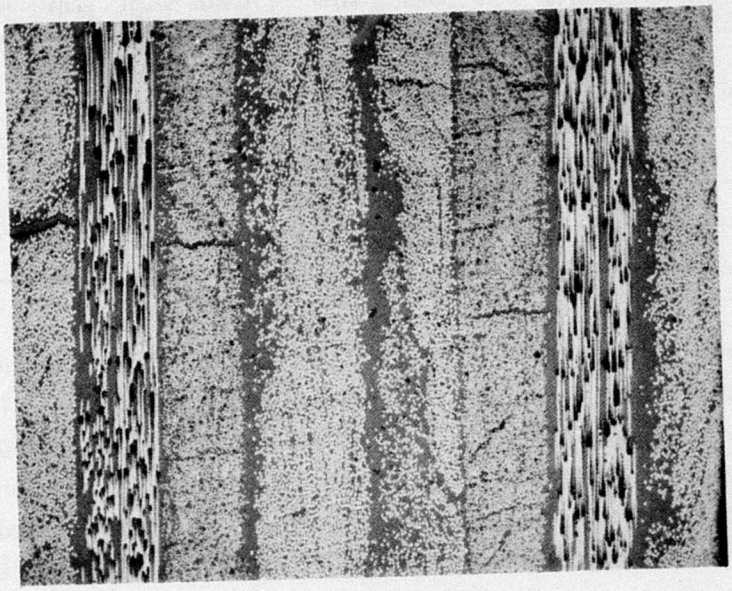


Figure 7. Pseudo-Isotropic Composite Panel 15-Inch By 15-Inch

aluminum alloy of 6.1 lbs/ft^3 density. The panels were vacuum bag molded as a one-stage cocured assembly using the HME resin in the outer skins to provide the bond to the honeycomb core. Several processing variables were screened prior to selecting the molding procedure used to fabricate test panels. These variables included brush-coating the honeycomb core with HME resin with and without a thixotropic filler, variations in volatile level of the HME/A-S prepreg tape, use of MEK *vs* acetone as the solvent for preparing HME resin and perforated *vs* nonperforated caul plates. Based on the results of these studies (see Table 10), the following fabrication procedure was used to prepare honeycomb sandwich panels for testing.

Prepreg tape was prepared from HME resin in acetone solution and Hercules A-S graphite fiber tow by the procedure described in Section 3.1. The volatile content of the HME/A-S prepreg was <1% by weight. Honeycomb core was cut to the required size using a sharpened putty knife, washed with water to remove excess debris and dried at 120°F in an air circulating oven. The core was cleaned in a trichloroethylene vapor degreasing bath and dried at room temperature. The core faying surface then was brush coated with the same resin varnish used in the prepreg tape.

Photomicrograph 45°



Photomicrograph 90°

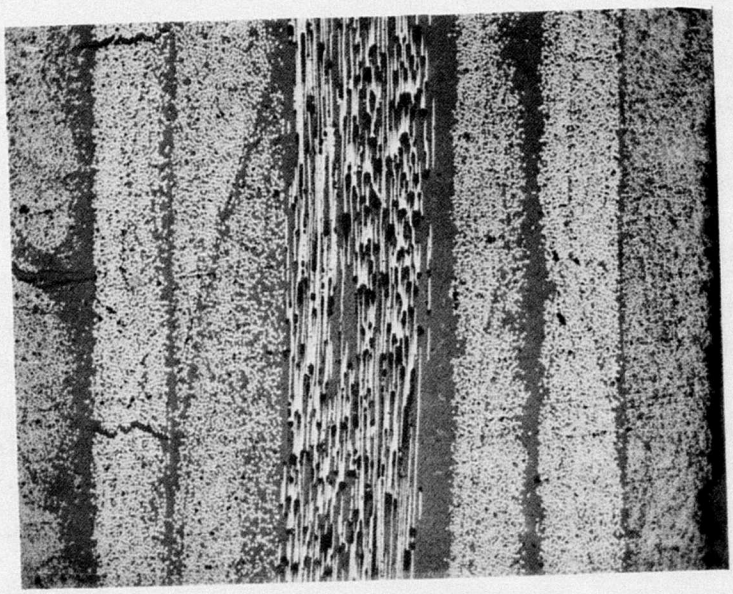


Figure 8. Photomicrographs Of Large Pseudo-Isotropic Multidirectional Panel

TABLE 10.

FLATWISE TENSILE STRENGTH OF HONEYCOMB PANELS

Resin Formulation For Brush Coating Honeycomb Core	Laminating Resin Solvent/Cooking Cycle	Flatwise Tensile Strength, psi	Failure Mode
HME[a)]	Acetone/45 mins at 136°F	590	Adhesive
HME with 5% w.w Cab-O-Sil	Acetone/45 mins at 136°F	210	Adhesive
HME	MEK/30 mins at 176°F	130	Adhesive
HME	MEK/45 mins at 176°F	180	Adhesive
HME	Acetone/15 mins at 136°F	450	Adhesive
HME	Acetone/45 mins at 136°F	345	Adhesive

a)See Table 8.

A four-ply lay-up of 0°, 90°, 90°, 0° configuration with the 0° in the honeycomb ribbon direction was used for each facing skin. The four plies of prepreg were placed on the top and bottom of the coated core and nonporous glass reinforced Teflon coated fabric was used between the prepreg and style 181 glass fabric (see Figure 9). A nonperforated caul plate was placed on top of the lay-up. Pieces of angle iron were cut to the height and dimensions of the honeycomb core and placed around the lay-up to prevent core crushing. The lay-up then was bagged using nylon film (green Vac Pac) and approximately 14 psia vacuum bag pressure was applied. The lay-up was placed in an air circulating oven, heated to 350°F at 3-5°F/minute and cured for 60 minutes at 350°F. After removal from the vacuum bag the sandwich panels were postcured for 16 hours at 400°F.

The resultant panels had good appearance and displayed very little skin dimpling (see Figures 10 and 11). In order to demonstrate the suitability of this molding process for fabricating structural panels with an edge close-out, a small demonstration panel was fabricated. This panel consisted of the same skin configuration as the test sandwich panels with a 2t : t edge close-out section (see Figure 12). No problems were encountered in fabricating this panel (see Figure 13). Following the successful demonstration of the one-stage, cocure vacuum bag molding process for HME/A-S honeycomb sandwich panels, a detailed evaluation of the resultant panels was performed (see Section 3.3).

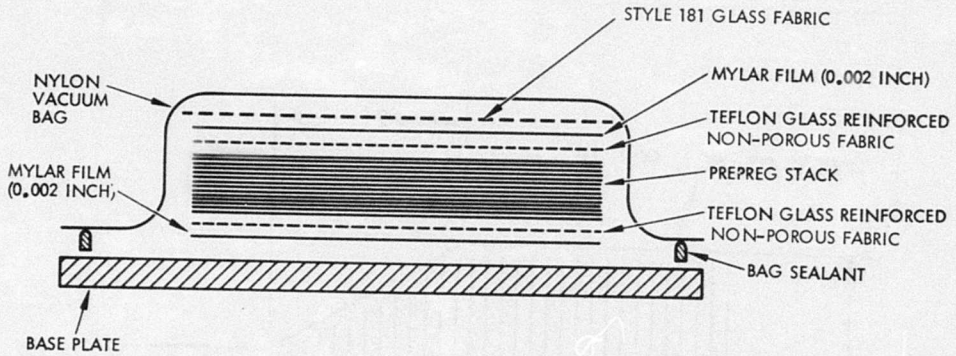


Figure 9. Sandwich Panel Fabrication

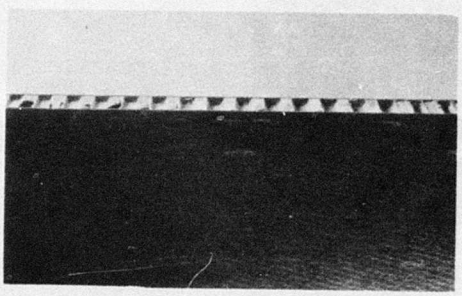


Figure 10. Overview Photo Of Honeycomb Test Panel

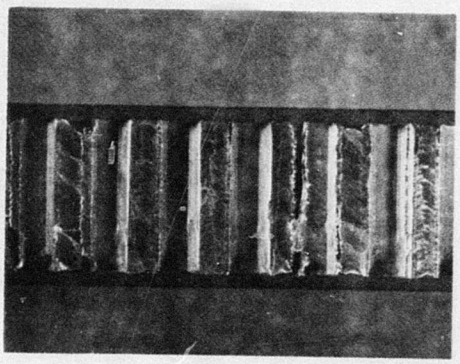


Figure 11. Close-up Photo Of Honeycomb Test Panel At Edge

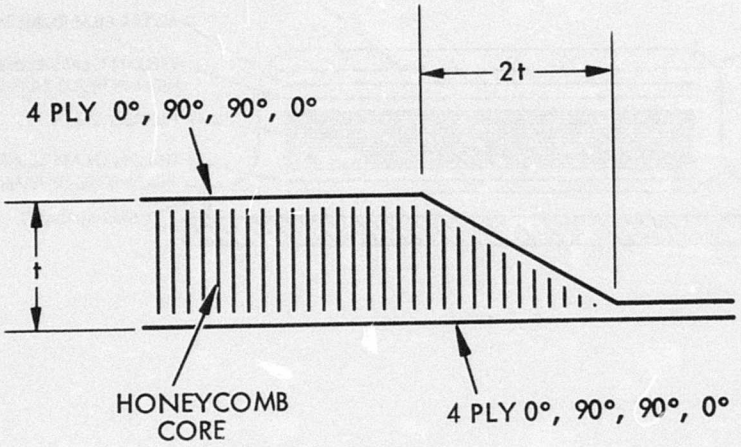


Figure 12. Demonstration Sandwich Panel

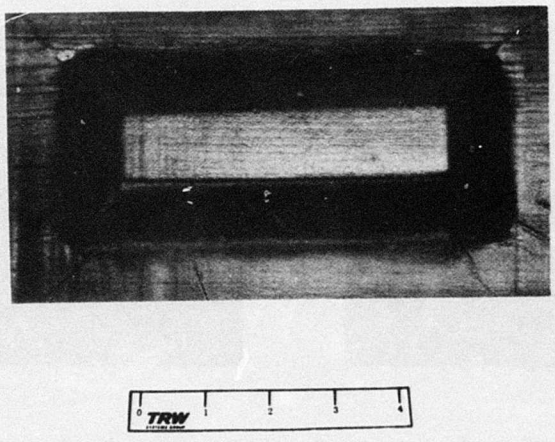


Figure 13. Photograph of Demonstration Sandwich Panel

3.3 DETAILED EVALUATION OF PANELS

The unidirectional and pseudo-isotropic composite panels described in Section 3.1 and the sandwich panels described in Section 3.2 were tested in order to provide preliminary structural property data on the HME resin. Details of the test procedures used during these evaluations are provided in the Appendices. Evaluation of the unidirectional vacuum bag molded HME/A-S composite panels (see Table 11) showed that the initial as-molded properties are equivalent to autoclave molded epoxy composites. For example, Hercules reports a flexural strength value of 209.2 Ksi for their autoclave molded type 2002A prepreg (Reference 4), which is within experimental error, *i.e.*, 3% of the value reported for vacuum bag molded HME/A-S prepreg (see Table 11). The strength retention at 275°F for the HME/A-S composite was 74% compared to 72% at 180°F for the Hercules 2002A.

TABLE 11.

HIGH HUMIDITY AGING OF UNIDIRECTIONAL HME/A-S COMPOSITES

Property	Initial	After 30 Days 95% RH, 120°F	Retention, %
Flexural Strength, Ksi			
at R.T.	204	187	92
at 275°F	148	140	95
Strength Retention, %	73	75	-
Shear Strength, Ksi			
at R.T.	10.1	9.7	97
at 275°F	7.0	7.5	107
Strength Retention, %	7.0	77	-
Weight Change, %	-	+0.3	-

This indicates that the HME resin may be used at a 95°F higher service temperature than Hercules 2002A under identical loading conditions.

Evaluation of the unidirectional HME/A-S composite after 30 days exposure in a 95% RH, 120°F environment showed no significant loss in mechanical properties (see Table 11). For example, strength retention values ∿92 to 107% were obtained which are higher than the strength retention of Fiberite 904 epoxy resin (see Figure 14) obtained under

a NASA program at General Dynamics Corporation (Reference 5). These data indicate that the HME resin is highly moisture resistant.

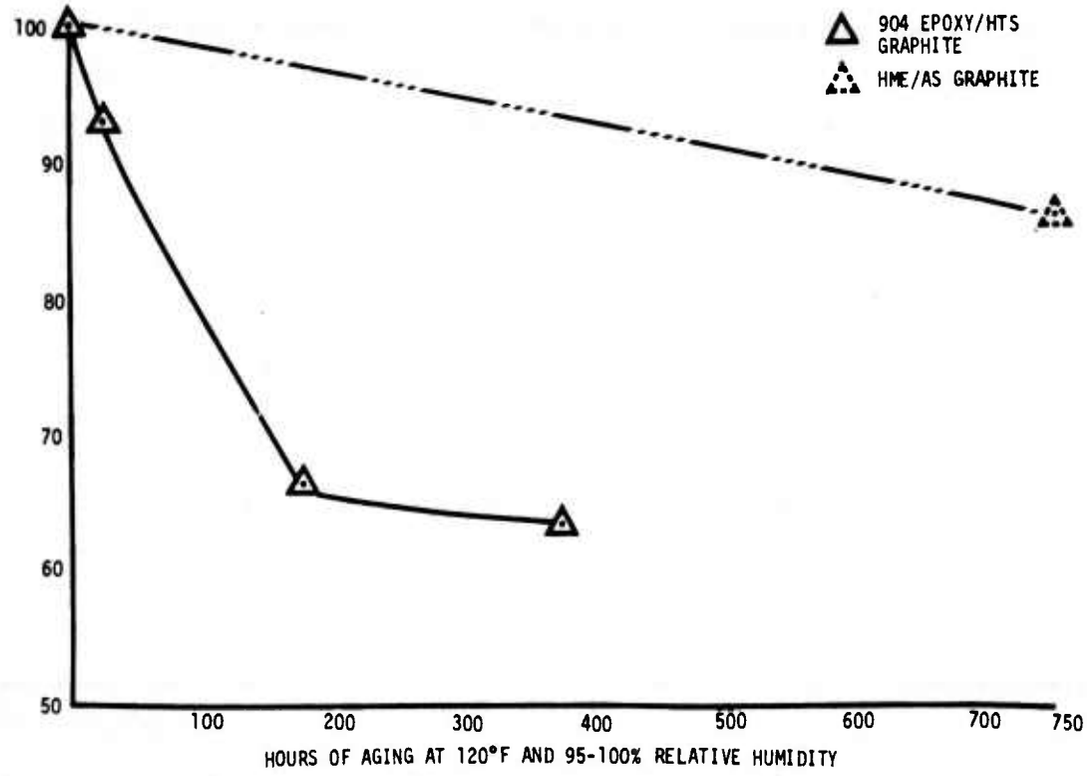


Figure 14. Comparison Of HME And Epoxy Resin Composites After High Humidity Exposure

The pseudo-isotropic HME/A-S composite panels were tested in the as-molded condition (see Table 12) and then after high humidity (see Table 13) and 350°F air (see Table 14) exposures. Testing at 275°F provided similar strength retention values to the unidirectional composite panels (see Table 11). Strength retention after 30 days exposure in a 95% RH, 120°F environment (see Table 13) were identical to those obtained for the unidirectional panels (see Table 11). An increase in strength was observed after aging for 30 days at 350°F in air (see Table 14), which indicates that further cure of the HME resin occurs during extended postcure at 350°F.

TABLE 12.
INITIAL COMPOSITE PANEL[a] PROPERTIES

Property	Specimen Orientation		
	0°	45°	90°
Flexural Strength, Ksi			
at R.T.	70.5	56.7	20.7
at 275°F	41.2	37.0	14.8
Flexural Strength Retention, %	58	65	72
Flexural Modulus, Msi			
at R.T.	8.1	5.0	1.7
at 275°F	7.0	4.2	1.3
Flexural Modulus Retention, %	87	84	76
Shear Strength, Ksi			
at R.T.	3.2	-	-
at 275°F	2.2	-	-
Shear Strength Retention, %	67	-	-
Tensile Modulus, Msi			
at R.T.	4.9	4.7	4.6
at 275°F	4.1	4.1	4.3
Tensile Strength, Ksi			
at R.T.	45.8	43.5	44.0
at 275°F	44.7	46.2	42.2
Composite Physical Properties			
Resin Content, w/w%		34	
Fiber Volume, v/v%		55	
Specific Gravity		1.45	
Void Content, v/v%		4	

[a] Pseudo-isotropic 8-ply 0°, +45°, -45°, 90°, 90°, -45°, +45°, 0° panel.

TABLE 13.

PHYSICAL PROPERTIES OF PSEUDO-ISOTROPIC MULTIDIRECTIONAL PANEL AFTER 30 DAYS AGING AT 120°F AND 95% HUMIDITY

Flexural Strength, Ksi[a)]	Initial	30-Day Humidity Exposure	Retention %
at R.T.	70.5	66.3	94
at 275°F	41.2	45.7	100

a)Samples cut in 0° direction of the 8-ply pseudo-isotropic 0°, +45°, -45°, 90°, 90°, -45°, +45°, 0° panel

TABLE 14.

PHYSICAL PROPERTIES OF PSEUDO-ISOTROPIC MULTIDIRECTIONAL PANEL AFTER 30 DAYS AGING AT 350°F IN AIR

Flexural Strength, Ksi[a)]	Initial	30-Day at 350°F	Retention %
at R.T.	70.5	83	118
at 275°F	41.2	57	138

a)Samples cut in 0° direction of the 8-ply pseudo-isotropic 0°, +45°, -45°, 90°, 90°, -45°, +45°, 0° panel

The honeycomb sandwich panel described in Section 3.2 was tested to provide information pertaining to the adhesive strength of the core to skin bond and to demonstrate correlation between sandwich panel skin and composite panel strength. Flatwise tensile tests were performed to evaluate the skin to core bond strength (see Table 15). Results from this evaluation demonstrated that the cocured HME/AS aluminum honeycomb core sandwich panel has equivalent flatwise tensile strength to secondary bonded sandwich panels. The flexural tests produced the expected mode of failure (see Table 15) and

the strength values obtained are of the order expected for high performance epoxy composites. These high skin strength values are attributed to the absence of severe dimpling in the HME/AS sandwich panel skins, which provides good correlation to flat composite panels.

TABLE 15.

HONEYCOMB SANDWICH PANEL PROPERTIES

Property	Test Temperature °F	Value	Mode of Failure
Flatwise Tensile Strength, psi	R.T.	325	Adhesive
Sandwich Flexural Strength, Ksi	R.T.	20.4	Compression
	275	9.1	Adhesive

IV. CONCLUSIONS AND RECOMMENDATIONS

It was concluded from the results of this effort that the HME resin developed during this program provides moisture resistant structural composites and sandwich panel structures suitable for 275°F service. The procedure developed for preparing the HME resin from a stable prepolymer was demonstrated to yield excellent reproducibility between batches. Furthermore, prepreg tapes produced by impregnating Hercules AS graphite fiber with an HME resin solution possessed excellent tack and drape. These prepregs were vacuum bag molded at 350°F to yield composite and sandwich panels with very low resin flow occurring during cure. It is apparent that the HME resin developed during this program is ready for evaluation in fabrication of large surface area composite panels for flight hardware intended for 275°F service.

Recommended further work with the HME resin includes:

- Demonstrate scale-up of HME resin varnish manufacture for use by commercial prepreg manufacturers.
- Demonstrate preparation of hot-melt HME resin and prepreg.
- Develop a modified HME resin formulation that yields composites suitable for 350°F service.

The above scale-up demonstration for resin manufacture is necessary in order to define processing times for large resin batches and to provide resin reproducibility data. Use of the HME resin as a hot melt resin is highly feasible because the intermediate elastomeric epoxy-polybutadiene prepolymer is a stable thermoplastic material. It is highly desirable to perform the HME hot-melt technology demonstration because many of the major prepreg manufacturers have tape production facilities which are limited to hot-melt processing. Modification of the HME resin formulation to provide 350°F service can be achieved by forming a cross-link network around the polybutadiene segment of the polymer. This can best be accomplished most simply by increasing the number of functional epoxy groups in the prepolymer. However, it is important to retain a major portion

of the polymer structure as polybutadiene because this provides the resin's hydrophobic character. Several novel approaches for modifying the HME resin have been identified and proposed to the Air Force.

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APPENDIX A.

TEST PROCEDURES FOR CHARACTERIZATION AND TESTING OF GRAPHITE TAPE, COMPOSITES AND HONEYCOMB SANDWICH PANELS

A.1 RESIN AND GRAPHITE TAPE CHARACTERIZATION

A.1.1 Prepolymer Acid Number

The acid number of the prepolymer indicates the extent of reaction between the epoxy resin and the terminal carboxy groups of the butadiene. The procedure for the determination of acid number is as follows:

> Resin varnish containing a 2.5 to 5g solids sample is transferred to a 300 ml Erlenmeyer flask. Two drops of 1 w/w% (in ethanol) phenolphthalein indicator are added to the flask. The solution then is titrated with 0.5 NaOH, while being vigorously stirred with a magnetic stirrer. The end point of the reaction is determined when the pink color persists for at least 30 seconds. The acid number is calculated as follows:

$$\text{Acid Number (milligrams KOH/g sample)} = \frac{V \times N \times 56.1}{W}$$

Where:

V = Volume of KOH solution for sample titration, ml
N = Normality of KOH solution
W = Weight of sample, g

A.1.2 Volatile Matter

Volatile content of graphite prepreg was determined by thermally treating a tarred sample for 30 minutes at 350°F. After cooling to R.T., the specimen was reweighed and the volatile content was calculated by the following formula:

$$\text{Volatile Content} = \frac{W_1 - W_2}{W_1} \times 100$$

Where:

W_1 = Weight Sample

W_2 = Weight Sample After Heat Aging

A.1.3 Resin Content

Resin content was determined by soxhlet extraction using acetone as the solvent. A weighed sample was placed in the soxhlet extraction apparatus and the solvent was heated to reflux until the solvent surrounding the extraction thimble became clear. The sample then was reweighed and the resin content was calculated by the following formula:

$$W_{wr} = \frac{W_2}{W_1} \times 100$$

$$W_{dr} = \frac{W_2 - VW_2}{W_1 - VW_2}$$

Where:

W_{wr} = Wet Resin Content

W_{dr} = Dry Resin Content

W_1 = Weight Sample

W_2 = Weight Sample Lost

V = Volatile Matter Content of Graphite Tape, Fraction

A.2 COMPOSITE CHARACTERIZATION

A.2.1 Graphite Composite Resin Content

The resin was digested from the cured sample by pouring acid (9:1 v/v concentrated H_2SO_4 - concentrated HCl) onto the sample in a glass beaker and then heating the acid until it turned black. At this point, 30% hydrogen peroxide solution was added dropwise to the acid until it turned clear again. The acid was reheated for a minimum of one hour. During this period, further drops of hydrogen peroxide solution were added to clear

the acid whenever the acid turned black. Upon completion of this cycle, the acid was cooled to room temperature and an additional 2 ml of hydrogen peroxide solution was added. The solution was heated again until white fumes appeared, after which it was cooled to room temperature. The acid was decanted from the filaments using a fritted glass filter, washed first in distilled water and then in acetone, after which the filaments were dried for 15 minutes in a 350°F air circulating oven. Resin solids contents were calculated:

$$W_r = \frac{(W_1 - W_2)}{W_1} \times 100$$

Where:

W_r = Weight Content of Resin Solids, % w/w

W_1 = Weight of Cured Composite Sample

W_2 = Weight of Filaments After Acid Digestion of the Resin Matrix

A.2.2 Density of Composites

Density of composites was determined from measured volumes (water displacement) and weights of specimens.

A.2.3 Composite Fiber Volume

Fiber volume percent of the composites was calculated by the formula:

$$V_f = 100\ (1-K)\ \frac{D_c}{D_f}$$

Where:

V_f = Volume Percent Fiber, %

D_c = Measured Density of Composite, g/cm^3

D_f = Density of Fiber, g/cm^3

K = Weight Fraction, Resin

The specific gravity of the Courtaulds A-S fiber is 1.76 g/cm^3.

A.2.4 Composite Void Content

Void contents of the composites were calculated using the formula:

$$V_v = 100 - D_c \left[\frac{W_r}{D_r} + \frac{W_f}{D_f} \right]$$

Where:

V_v = Volume of Voids, % v/v

D_c = Measured Density of Composite, g/cm^3

D_r = Density of Resin, g/cm^3

D_f = Density of Fiber, g/cm^3

W_r = Weight Content of Resin, %

W_f = Weight Content of Fiber, %

A.2.5 Shear Strength of Composites

The cured composites were machined into short beam shear specimens 0.25-inch wide x 6 times the specimen depth in length and tested in flexure loading point using a 4:1 span to depth ratio. Loading rate was .05-inch/minute.

Shear strengths were calculated using the simple formula:

$$S_u = \frac{0.75V}{tb}$$

Where:

S_u = Ultimate Shear Strength, psi

V = Load at Failure, lbs.

t = Specimen Thickness, Inches

b = Specimen Width, Inches

A.2.6 Flexural Properties of Composites

The cured composites were machined into flexural specimens 0.5-inch wide by 4-inch long and tested in flexure at a two point loading at quarter span joints using a 32:1 span-to-depth ratio. Loading rate was 0.05-inch/minute.

Flexural strengths and moduli were calculated using the formuli:

$$F_u = \frac{3PL}{4Bd^2}$$

and

$$E_b = \frac{L^3 m}{8Bd^3}$$

Where:

F_u = Stress in the Outer Fiber at Mid-span, Ksi

E_b = Modulus of Elasticity in Bending, Msi

P = Load at Failure, lbs

L = Span, Inch

b = Width of Specimen, Inch

d = Thickness of Specimen, Inch

m = Slope of the Tangent to the Initial Straightline Portion of the Load Defelection Curve, lbs/in.

A.3 HONEYCOMB SANDWICH PANEL CHARACTERIZATION

A.3.1 Flatwise Tensile Strength of Sandwich Panels

Flatwise tensile strength was determined according to the method described in MIL-STD-401B using 2-inch by 2-inch specimens. These were machined from a cocured honeycomb sandwich panel which had 4-ply 0°, 90°, 90°, 0° skins with the ribbon direction of the honeycomb in the 0° direction.

A.3.2 Sandwich Flexure Testing

Flexure testing was performed on the sandwich panels according to MIL-STD-401B using 11-inch long (honeycomb ribbon direction and 0° skin direction) by 1.75-inch wide specimens. The average facing stress was determined using the formula:

$$F = \frac{P_B \; a_B}{4 \; t(d + t_c)b}$$

where F = facing stress

P_B = total force, applied at 2 points located at a distance of $a_B/4$ from each reaction

a_B = span length

t = facing thickness

d = total sandwich thickness

t_c = core thickness

b = sandwich width

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